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**ELECTRONICS**

# POTENTIAL USES OF THE STRESS– AND RUPTURE–INDUCED OPTICAL EMISSION EFFECT IN POLYMERS

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*Dedicated to the memory of Cristofor Simionescu*

We review the stress- and rupture-induced optical emission effect with special reference to adhesives and polymers used in adhesives. We add new considerations on the mechanisms producing this effect and also add remarks on the methods for its measurement in view of engineering applications of adhesives.

*Keywords*: stress-induced luminescence, optical emission, adhesives, optical emission measurement

## 1. INTRODUCTION

Large progresses have been made during the last few decades in understanding the adhesion processes and in using adhesives in medicine, biotechnology, material science, electronic engineering, aerospace and automotive engineering, among others. Molecular adhesion bonds play an essential part in biology [1] and in many technology branches, as a major interfacial contact binding force. Other mechanisms contributing to joining through adhesives are mechanical interlocking (keying), diffusion in the substrate [2], electronic (electrostatic) binding, and adsorption forces [3]. Molecular adhesion bonds may include electronic forces, permanent dipole-dipole, such as hydrogen bonds involving or not fluorine and other non-hydrogen dipole-dipole bonds, dipole-induced dipole, and London (dispersion) forces, which are interactions of mutually induced dipoles (induced dipole-induced dipole attraction, a very weak force) [1,4]. On the other side, the forces inside the interface (in the adhesive), sometimes named intrinsic adhesion forces, should be equally large [3] for a good joint.

The effect of stress- and rupture-induced optical emission in polymers was experimentally discovered by the author of the present study in 1985, in connection with parallel studies on liquid crystal photoelastomerty (first reported in 1982, [5]) and on other novel methods for stress analysis [6–9]. The finding came accidentally when I was trying to produce charging at fracture at the bonding place of glass, plexiglass and other plates bonded with adhesives, and at the bonding of plates with adhesive tapes. The experiments resulted in some charging, but also in light emission. The last effect was naturally named stress- and rupture-induced optical emission (in adhesives) and then reported in [9][1]. Optical emission (OE) may be produced as a result of rupture or of the effect of 'tribocharging', followed by electrostatic discharge in the air, or of a combination of these effects. For now, the precise cause or combination of causes that produces the OE effect is still unclear. It turns out that a similar effect should be produced during friction by the fracture of micro-wrinkles of surfaces [10], when the surfaces under friction contain certain polymeric chains that, either by rupture or by the effect of 'tribocharging' electrostatic discharge, are able to free enough energy to produce infrared (IR), visible, or ultraviolet (UV) radiation (with a potential between 3 to 12 kV, as evidenced for example in [11]).

The applicative study of the stress- and rupture-induced optical emission in polymers was not pursued. In this brief paper, we bring forth a few theoretical and applicative considerations and speculate on the potential uses of such effect.

## 2. APPLICATIVE POTENTIAL OF STRESS – AND RUPTURE – INDUCED OPTICAL EMISSION

Adhesives, such as the epoxidic ones, are increasingly used for joining parts in manufacturing, and are frequently replacing welding of metal parts in the automotive industry. In many applications they are used due to their good thermal conductivity and electrical insulation, combined with excellent heat resistance [12]. Also, adhesive tapes (pressure sensitive tapes) have found innumerable applications, some of them demanding high adhesion values, measured as both tensile force and shear force. In these applications, measuring the strength of adhesion and understanding the mechanisms of separation of the bonded surfaces at the level of the adhesive layer are imperative for improving the adhesives.

Most measurements today are unable to determine when the bonds start to degrade and micro-fractures start to appear in the adhesive layer. It is in these niche applications that the stress- and rupture-induced optical emission is most suitable.

### 2.1. MECHANISMS OF DEGRADATION IN ADHESIVE LAYERS

There is no doubt that, in many cases, separation of the bodies bond by an adhesive layer is produced by its fracture, as proved by the material left on both surfaces after separation at the same point. In contrast, the mechanism of separation

[1] That paper is the only one, unfortunately for me, I co-authored with the great chemist Cristofor Simionescu, who made extremely valuable remarks on the phenomenon. Professor Cristofor Simionescu has suggested at that time that the method should be further investigated at the "P. Poni" Institute Macromolecular Chemistry of the Romanian Academy, but I am not aware of such a research. Maybe this short paper will incentivize young researchers to study and apply this effect which still is, technically speaking, at its infancy regardingito the applications.

of the adhesive from a single surface, that would imply preservation of the integrity of the adhesive layer, occurs only in some cases.

The third mechanism involves fracture of the adhesive layer with material remaining only on one surface, with islands of material left on both surfaces, but not at the same place. This is produced rarely, when non-uniform adhesion to surfaces occurs. This mechanism implies fracture of the adhesive layer limited to closed boundaries, but not in the thickness of the layer.

The effect of stress- and rupture-induced optical emission in polymers may be related to the strongest molecular binding forces, possibly involving the electronic and dipolar attraction forces. A theory on unbonding of the molecular bonds was developed by Evans and Ritchie [1], following Bell (cited by Evans) and Hanggi *et al*. [13]. Evans and Ritchie [1] recall that "*rupture strengths for weak bonds are not constants but instead depend on the rate of force application and duration of loading*", a fact well-known in adhesive technology.

The frequency of radiation, $\upsilon_R$, is given by the molecular bonding energy, $E_b$, according to:

$$h\nu_R \le E_b,\ \nu_{R\,max} \le \max_j (E_{bj})/h$$

where $h$ is Planck's constant, $E_{bj}$ are the bonding energies of species $j$ in the adhesive and substrates, and the less than sign is due to energy dissipation by multiple effects (typically, internal body heat) beyond radiation. Therefore, the spectrum of the radiated energy in the discussed effect is informative on what bodings are broken in the process. In addition, following the model proposed by Evans and Ritchie [1], the off rate, $\upsilon_0$, which is an indicator of the probability of molecular unbonding, is given by:

$$\upsilon_0 \sim \omega_0 e^{-\frac{E_b - f x_b}{k_B T}}$$

where $\omega_0$ is the natural vibration frequency of the bond in vacuum, $f$ is the applied force on the unbinding molecules, $x_b$ is the displacement between the molecules, the product $fx_b$ is the mechanical energy transferred to the molecules by the force, that is, the disjoining potential, $k_b$ is Boltzmann constant and $T$ – absolute temperature. Thus, the probability of off-binding increases rapidly with the deformation of the adhesive; deformation increases the disjoining potential because of the large $x_b$ values. Once the disjoining potential is large enough, the bond is broken. Yet, as the attractive potential in the bond decreases with distance, the released energy decreases when $x_b$ increases. Therefore, combination of the two factors seems to indicate an optimal value $x_b$, where radiation generation is most probable.

### 2.2. TESTING THE ADHESION STRENGTH OF PRESSURE SENSITIVE TAPES

Determining the relationship between the (transparent) optical emission effect and the force parting the tape from the substrate under traction forces applied at various angles and at various velocities of movement of the separation line on the tape is straightforward. It suffices to film the process at dark, when applying an increasing pulling force. This method, reported in [7-9], is sketched in Figure 1 (a). When the des-joining line moves too slowly, that is, when the separation process is slow, no emission may be observed. Notice that the method may not work for any type of adhesives. We have not tested silicone adhesives. Figure 1 (b) shows how to apply the method, using at least one transparent sample, for pull-off adhesion tests.

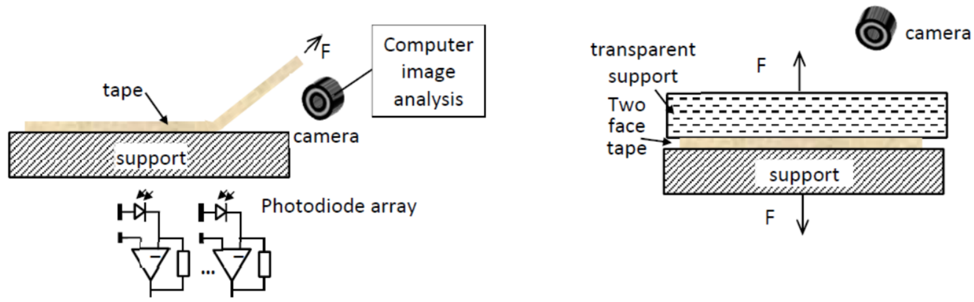


Fig. 1. Micro-fracture detection in the adhesive layer for pressure sensitive (adhesive) tapes. (a) For oblique traction forces applied at various angles to the tape; (b) double side, transparent tape with at least on support transparent.

A camera or a set (array) of photodiodes with suitable circuitry (transimpedance amplifiers – see, for example [14]) is easy to adapt to the experiment, to measure the optical signals produced by the effect (Fig. 1). Notice that the camera has to be a high sensitivity one, and should be chosen so that to have a high responsivity in a wide bandwidth (IR, visible and UV radiation). Also, the camera and the photodiode array, whichever is used, should have a fast response time, because the microscopic light emission is expected to be very fast (nano- to microseconds). Large response times produce an equivalent integration over the response time, which reduces the sensitivity with misses of small flashes and the integration of several such flashes, that are no more counted as distinct. Computer-based image analysis of the pictures of the stress- and rupture-induced optical emission could reveal valuable details of the joint rupture process.

### 2.3. OPTICALLY TESTING THE ADHESION STRENGTH OF ADHESIVES BETWEEN TWO PARTS

Testing of adhesives for the detection of micro-fractures, when the adhesive is bonding two surfaces, can be done similarly to the case of adhesive tapes, conditioned by the use of at least one transparent bonded body. The camera can be external, as in Figure 1, or it may be incorporated in the bonded part, that is transparent. Another possibility for further study is to incorporate in the transparent bonded part a bundle of optical fibers that conduct the radiation to the camera. This solution may have the advantage of lower cost, as the camera is reusable. However, the use of fiber optics modifies the adhesion properties to the substrate in which they are included and limits the visibility of radiation to the "opening angle" of the fibers, thus reducing the collected light.

### 2.4. TESTING THE ADHESION STRENGTH OF ADHESIVES BETWEEN TWO PARTS BY THE ELECTRICAL FIELDS CREATED

Either the effect of stress and adhesive layer rupture is triboelectric electrical charging or macromolecules rupture, a charge is locally generated. Using recent methods of computing charge density by means of the potentials it creates at some distance (for example, at the borders of the sample), one can detect changes in the surface charging of the sample and can thus derive the map of charging. This method was not yet tested, but seems promising because of the progresses made in charge and impedance tomography. Procedures based on charge density tomography have been recently established and can be used to create accurate charge maps [15–18]; therefore, the charge induced by the rupture of molecular bonds and of polymer molecules in the adhesive can also be applied today, as an alternative to optical detection.

## 3. DISCUSSION AND CONCLUSIONS

The effect of stress- and rupture-induced optical emission in adhesives is new, but optical emission at rupture of crystals was known for a long time [19]. Zink, Hardy and Sutton [20] reported in 1976 on the spectra of the light emission from several mono- and disaccharides and concluded that the adsorbed and absorbed nitrogen is excited in the process. They contest the hypothesis that electrical discharge is the cause of nitrogen excitation. They recall that the optical emission produced in mechanically stressed saccharides were reported by Bacon and Boyle; Boyle was the first to study emission under vacuum and he concluded that electrical discharge plays no role. In [20], the authors prove that that conclusion was not allowed by Boyle experiments, because of the adsorbed and absorbed nitrogen on the surfaces (Boyle has not degassed the surfaces, as [20] did). In [20], it is stated that a minimal energy of 11 eV is needed to excite molecular nitrogen (starting from the ground state to the $^3\pi_u$ ).

An optical emission effect was proved recently when scratching of an inorganic insulator surface with a diamond, by Miura and Nakayama [21]. In contrast with [20], they support the view that the electric charging produced during scratching and the discharge in air are responsible for the light emitted: "*spectra showed ... sharp peaks in the ultraviolet region ... [that]... were perfectly matched to those for the second positive band of N2, demonstrating that an electric discharge of N2 gas occurred at the frictional contact*". However, it seems that their experiments were less carefully conducted than those reported in [20].

There are numerous studies of optical emission at rupture, issued especially after 1990; for example, Li and Haneman [22] proved that an optical emission effect is produced at natural fiber rupture. It was only in 2007, at our best knowledge, that the second paper on the optical emission effect in adhesive was published (by Miura [23]). An interesting contribution, because it proves a strong, usable effect, is due to Jeong *et al*. [24].

The method of stress- and rupture-induced optical emission could be a valuable addition to the existing handful of tools for determining the bonding strength of adhesive tapes and adhesive bonds between parts. The optically clear adhesives are especially better suited for the use of this method; however, due to the very low thickness of the adhesive layers, transparency is not essential for the method.

The today very low price of the imaging devices combined with good software tools to automatically monitor the changes in pictures makes the method of stress- and rupture-induced optical emission competitive with other methods and even more precise than the traditional procedures of analysis of the attachments by polymeric adhesives under stress. The method may find uses in various fields, including aeronautics, electronics, and medicine, where the bonding quality is highly demanding.

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